Photo-reactivity of surfactants in the sea-surface microlayer and subsurface water of

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Abstract

We report the first estimates of total surfactant photo-reactivity in the sea-surface microlayer (SML) and in subsurface water (SSW) (Tyne estuary, UK; salinity 0.3-32.0). In addition to temperature, a known driver of surfactant adsorption kinetics, we show that irradiation contributes independently to enhanced interfacial surfactant activity (SA), a notion supported by coincident CDOM photodegradation. We estimate a mean SA production via irradiation of 0.064 \pm 0.062 mg l-1 T-X-100 equivalents h-1 in the SML and 0.031 \pm 0.025 mg l-1 T-X-100 equivalents h-1 in the SSW. Using these data, we derive first-order estimates of the potential suppression of the gas transfer velocity (kw) by photo-derived surfactants ~12.9-48.9%. Given the ubiquitous distribution of natural surfactants in the oceans, we contend that surfactant photochemistry could be a hitherto unrecognized additional driver of air-sea gas exchange, with potential implications for global trace gas budgets and climate models.

1	Photo-reactivity of surfactants in the sea-surface microlayer and subsurface water of
2	the Tyne estuary, UK
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10	Key Points:
11	• Irradiation results in increased surfactant activity in the sea-surface microlayer and in
12	subsurface water in the Tyne estuary (UK)
13	• Surfactant activity increased in parallel to photodegradation of chromophoric dissolved
14	organic matter
15	• Insolation driven increases in sea-surface microlayer surfactant activity may have global
16	implications for air-sea trace gas exchange
17	
18	

19 Abstract

We report the first estimates of total surfactant photo-reactivity in the sea-surface microlayer 20 (SML) and in subsurface water (SSW) (Tyne estuary, UK; salinity 0.3-32.0). In addition to 21 22 temperature, a known driver of surfactant adsorption kinetics, we show that irradiation 23 contributes independently to enhanced interfacial surfactant activity (SA), a notion supported by coincident CDOM photodegradation. We estimate a mean SA production via irradiation of 0.064 24 \pm 0.062 mg l⁻¹ T-X-100 equivalents h⁻¹ in the SML and 0.031 \pm 0.025 mg l⁻¹ T-X-100 25 equivalents h⁻¹ in the SSW. Using these data, we derive first-order estimates of the potential 26 27 suppression of the gas transfer velocity (k_w) by photo-derived surfactants ~12.9-48.9%. Given the ubiquitous distribution of natural surfactants in the oceans, we contend that surfactant 28 photochemistry could be a hitherto unrecognized additional driver of air-sea gas exchange, with 29 potential implications for global trace gas budgets and climate models. 30

31

32 Plain Language Summary

Surface-active substances (surfactants) are ubiquitous in seawater and freshwater. They 33 accumulate in the uppermost $< 1000 \,\mu m$ (surface microlayer) where they slow the rate of gas 34 exchange between water and air. Improved knowledge of surfactant distributions and behaviour 35 will improve global gas flux estimates (e.g. for CO₂) used to inform climate models. While 36 increased temperature is known to enhance the microlayer accumulation of surfactants, further 37 slowing gas exchange, our knowledge of other potentially important processes (e.g. surfactant 38 photo-reactivity) is lacking. In the laboratory we simulated the natural solar irradiation of 39 estuarine waters (Tyne, UK), and found surfactant enhancement additional to that from increased 40 41 temperature, presumably reflecting photo-degradation of larger organic molecules. We argue that sunlight induced changes in other coastal waters, in the open ocean, and in freshwater will likely 42 43 reflect differences in their organic compositions, prompting a need for wider investigation of this process. 44

45 **1 Introduction**

The sea surface microlayer (SML) impacts global element cycling and climate through the
production, removal, and air-sea exchange of climate-active gases (Upstill-Goddard et al., 2003;

Cunliffe et al., 2013; Carpenter & Nightingale, 2015; Engel et al., 2017), and by generating 48 marine boundary layer (MBL) aerosols (Facchini et al., 1999; Donaldson & George, 2012). 49 Natural surfactants that are ubiquitous in seawater are enriched in the SML (Sabbaghzadeh et al., 50 2017; Wurl et al., 2011) via their adherence to the surfaces of rising bubbles that are generated 51 during wave breaking (Robinson et al., 2019; Tseng et al., 1992), and which burst at the sea 52 surface. This reduces the air-sea gas transfer velocity (k_w) of CO₂ and other gases by up to 50% 53 (Frew, 2005; Salter et al., 2011; Pereira et. al., 2016; 2018), and following wind entrainment, 54 impacts the MBL aerosol inventory (Leck & Bigg, 1999; Ovadnevaite et al., 2011; Kroflič et al., 55 2018). 56

High UV irradiance promotes high SML photo reactivity. Correlations of SML total surfactant 57 activity (SA) with chromophoric dissolved organic matter (CDOM) absorbance (Sabbaghzadeh 58 et al., 2017) are consistent with surfactant photo-reactivity, by analogy with CDOM 59 photodegradation (Helms et al., 2008). Artificial surfactants produced volatile organics during 60 irradiations of laboratory grade water (Fu et al., 2015; Alpert et al., 2017; Bernard et al., 2016), 61 saline solutions (Ciuraru et al., 2015a, b), and artificial biofilms (Brüggemann et al., 2017). 62 While photochemistry involving SML surfactants likely modifies k_w and MBL chemistry, 63 photochemical changes to natural SML surfactants have yet to be unequivocally demonstrated. 64 We therefore irradiated (solar simulator) contrasting salinity samples from the River Tyne 65 estuary (UK), generating the first direct evidence for photochemical changes in SML SA. We 66 compared these data with simultaneous changes in subsurface water (SSW) SA, and with 67 68 corresponding changes in spectral CDOM characteristics, to evaluate the potential for air-sea gas exchange control by photochemically-derived surfactants in the SML. 69

70 2 Study Site and Sampling

The River Tyne (mean discharge $45 \text{ m}^3 \text{ s}^{-1}$) enters the North Sea via the 35 km long Tyne

estuary, which is macrotidal and partially mixed (Stubbins et al., 2010). We collected 13

estuarine samples (seven SML and six SSW: see supporting information) from four sites (TE1-

TE4; Figure 1) spanning 0.3-32.0 salinity between the estuary mouth and 28 km upstream. SML

rs sampling (June 2016 – January 2017) used a Garrett Screen (Garrett, 1965) (mesh: 16, wire

diameter: 0.36 μ m; effective surface area: 2025 cm²) according to standard procedures

(Gašparović et al., 2014) routine in our work (Pereira et al., 2016; Sabbaghzadeh et al., 2017).

Visual inspection prior to screen deployment precluded SML contamination by floating debris. 78 TE1 was accessed using waders, avoiding entrainment of resuspended sediments. TE2-TE4 79 required a support vessel (RV Princess Royal) with the Garrett Screen hand-deployed over-side, 80 minimizing potential contamination (engines off, wheelhouse and afterdeck downwind; Pereira 81 et al., 2016). Sample volumes ~15 ml per dip equated to a 65-80 µm sampling depth. Twelve 82 samples were unfiltered (supporting information) to retain SA associated with suspended 83 particles (Ćosović & Vojvodić, 1987; Ćosović, 2005; Pereira et al., 2016; Schneider-Zapp et al., 84 2013). To discern photochemically mediated changes in SA and CDOM absorbance from those 85 mediated by dissolved-particulate interactions and microbial processes, one sample (TE1; 30th 86 January 2017; supporting information) was split into 0.22 µm filtered (Millex-GP 87 polyethersulfone (PES) membrane) and unfiltered subsamples. For the irradiations we pooled 88 SML samples from ~65 repeat deployments at each site (1000 cm^3). SSW sampling (~20 cm 89 90 depth) used a clean 12-L steel bucket (Princess Royal) or 1-L polypropylene sample bottle 91 (TE1). Sample storage bottles (1-L polypropylene) were aged (leachable organics-free), prewashed (10% HCl acid; analytical grade water (milli-Q: $\geq 18.2 \text{ M}\Omega \text{ cm}$, Millipore System Inc., 92 USA)), and filled to overflowing to preclude any headspace. Transport (< 3 hours) and storage 93 pre-irradiation (< 48 hours) was at 4°C in the dark (Schneider-Zapp et al., 2013). 94





Figure 1 Tyne estuary (UK) sampling locations: TE4 (salinity 32.0) to TE1 (28 km upstream, salinity 0.3). Data from sites B1-B5 (Pereira et al., 2016) support our subsequent data interpretation. Colour bar indicates water depth (m). Map created with Ocean Data View: Schlitzer, R., https://odv.awi.de, (2018).

96

97 **3 Irradiation Experiments**

Irradiation experiments used a custom-designed solar simulator (Kitidis et al., 2008) and 98 established procedures (e.g. Stubbins et al., 2011; Uher et al., 2017). The irradiation source (300 99 W Xenon-arc lamp: LOT Oriel; 300 nm transmission cut off) was borosilicate glass-sleeved to 100 remove UVC radiation and surrounded by a motorized, 16 flask carousel. Total integrated 101 spectral irradiance (247.8 W m⁻²; 250-1050 nm; ILT950, LOT Quantum Design) exceeded mean 102 July daily surface shortwave radiation (280-850 nm) for Newcastle upon Tyne (150-200 W m⁻²; 103 Hatzianastassiou et al., 2005) but was in the range of in situ daily maximum Global Horizontal 104 Irradiance (GHI) during sampling (103.4-814.8 W m⁻²; supporting information; copernicus.eu/; 105 240-4606 nm; Qu et al., 2017). Three experimental protocols used pre-combusted (450 °C; ≥4 h), 106 50 ml quartz irradiation flasks: (i) irradiated samples (IS: solar simulator, 14 experiments); (ii) 107 dark controls (DC: double tin foil insulation, solar simulator, 14 experiments); (iii) temperature 108 controls (TC: double tin foil insulation, 4 °C storage, 8 experiments). Sampling was at 0, 2, 4, 6, 109 8 and 24 hours, with 0-hour samples assumed to represent in situ conditions. Analytical 110 111 constraints (irradiation duration, carousel spaces) precluded routine sample replication in individual experiments. We therefore replicated each experiment in full. Sample temperatures 112 (unfiltered: IS, 19.1-28.5 °C; DC, 17.0-24.6 °C; TC, 7.6-17.3 °C) were recorded immediately 113 prior to SA analysis. CDOM sub-samples were immediately filtered (0.22 µm PES) and 114 equilibrated to ambient temperature for 1 hour prior to analysis. 115

116

117 **4 SA and CDOM analysis**

All glassware was pre-combusted (450 °C; \geq 4 h), acid washed (10% HCl) and rinsed (Milli-Q) 118 between samples. SA was analyzed by hanging mercury drop, phase sensitive AC voltammetry 119 (797VA Computrace, Metrohm, Switzerland) (Ćosović and Vojvodić, 1998). Calibration was 120 against a nonionic soluble surfactant (Triton T-X-100 (Sigma-Aldrich, UK); mg L⁻¹ T-X-100 121 equivalents) in a 0.55 mol L^{-1} NaCl matrix. Samples were adjusted to the ionic strength of the 122 standards by adding NaCl solution (3 mol L^{-1}) to a maximum of 50 µL. Analytical precision was 123 typically better than $\pm 5\%$. We recorded CDOM absorbance (250-800 nm, 1 nm increments) on a 124 UV-Visible double beam spectrophotometer (M550: Spectronic Camspec Ltd., UK), using 0.01 125 m pathlength cuvettes and a Milli-O reference. We corrected for instrument drift, refractive 126

- index effects and light scattering by residual particles by subtracting the mean 650-700 nm
- sample absorbance (Kitidis et al., 2006). Absorption spectra were derived from: a = 2.303A/L
- 129 (Kitidis et al., 2006), where A is the offset corrected wavelength-dependent absorbance
- 130 (dimensionless) and L is optical pathlength (m). We adopted a_{300} (absorption coefficient at 300
- nm) as a CDOM concentration proxy (Bricaud et al., 1981; Hu et al., 2002), as in previous
- studies of coastal and oceanic waters (Helms et al. 2013; Kitidis et al., 2006; Sabbaghzadeh et
- 133 al., 2017).
- 134

135 **5 Derived quantities and statistical analysis**

- 136 We defined SA production during irradiation (mg L^{-1} T-X-100 eq. h^{-1}) as the difference between
- 137 SA in irradiated samples (SA_{IS}) and dark controls (SA_{DC}) over time (T; 2 or 24 hours): SA_{irr} =
- 138 $\frac{SA_{IS}-SA_{DC}}{\tau}$. The SA temperature effect was estimated as the difference between SA in dark
- 139 controls (SA_{DC}) and temperature controls (SA_{TC}) over time (T; 2 or 24 hours): SA_{temp} =
- 140 $\frac{SA_{DC}-SA_{TC}}{\tau}$. Following Helms et al. (2008), we derived CDOM spectral slopes (S; nm⁻¹) for the
- 141 wavelength ranges 275-295 nm $(S_{275-295}; \text{ nm}^{-1})$ and 350-400 nm $(S_{350-400}; \text{ nm}^{-1})$, using:
- 142 $a(\lambda) = a(\lambda_r)e^{-S(\lambda \lambda_r)}$ (Helms et al., 2008), where $a(\lambda)$ is the absorption coefficient (m⁻¹) at
- 143 wavelength λ (nm) and λ_r is a reference wavelength (nm). These spectral slopes and the resulting
- spectral slope ratios ($S_R = S_{275-295}/S_{350-400}$) were used as broad indices of CDOM
- characteristics, including source, molecular weight, and degradation history (Helms et al., 2008;
- 146 Kitidis et al., 2006).
- 147

All statistical procedures used SPSS. Data were screened for normality (Shapiro-Wilk tests), and correlations assessed using Kendall's-Tau correlation coefficient (null hypothesis: no significant SA vs CDOM correlation; significance 0.05) and the coefficient of determination ($R^2 \ge 0.5 =$ strong correlation).

152 6 Results

153 CDOM behaviour over 24 hours irradiation followed established trends (e.g. Fichot & Benner,

- 154 2012; Helms et al., 2008), with a_{300} pseudo first-order half-lives $(t_{1/2}) \sim 0.3-0.9$ d. In IS,
- 155 consistent increases in $S_{275-295}$ (6-29%) and S_R (12-35%) (supporting information) imply

irradiation induced decreases in CDOM molecular weight and aromaticity (Helms et al., 2008).

157 Changes in $S_{350-400}$ were negligible over time and between experimental protocols (supporting

158 information).

159

SA changes during irradiations indicated both photochemical and temperature effects in the SML 160 and in SSW (Figure 2). For 64 of 67 time-points SA_{IS} exceeded SA_{DC}, for all time-points (39) 161 SA_{IS} exceeded SA_{TC} , and for 38 of 39 time-points SA_{DC} exceeded SA_{TC} . The data thus confirm a 162 photochemical SA source in the Tyne estuary. The largest changes in SA_{1S} consistently occurred 163 during the initial 2 hours of irradiation and changes in both SA_{IS} and SA_{DC} were generally greater 164 in the SML (SA_{IS}: 0.10-0.40 mg L⁻¹ T-X-100 eq.; SA_{DC}: 0.03-0.40 mg L⁻¹ T-X-100 eq.) than in 165 SSW (SA_{IS}: 0.08-0.21 mg L⁻¹ T-X-100 eq.; SA_{DC}: 0.03-0.14 mg L⁻¹ T-X-100 eq.). In general, 166 SA_{IS} increased over 24 hours in both SML and SSW (Figure 2, *a,b,e,f,h,j-n*), although some 167 experiments showed overall decreases (Figure 2, c and d) or no discernable change (Figure 2, g 168 and i). Comparison of initial SA in unfiltered and 0.22 µm filtered SML subsamples from TE1 169 (Figure 2, g and h) indicated a significant particle contribution (40%). Importantly, SA_{IS} 170 increased in both subsamples during irradiation and remained higher than both SA_{DC} and SA_{TC}, 171 consistent with photochemical SA production. 172

173

As our experimental design precluded SML interaction with SSW or air the variable changes in 174 SA we observed (Figure 2) must reflect a dynamic balance between production and removal. To 175 clarify the overall extent of SA change we subsequently consider only those production rates due 176 to irradiation (SA_{irr}) and temperature (SA_{temp}) estimated over 0-2-hours (Table 1), the interval 177 for which the greatest SA changes were consistently observed. These estimates are reasonable 178 179 for our study area, for which total daylight ranged from ~7.5 hours (2 December 2016) to ~17.3 hours (27 June 2016) (supporting information). Although we also calculated SA_{irr} and SA_{temp} 180 over 0-24-hours (Table 1), these do not represent conditions in situ. 181 182

183 Mean SA_{*irr*} (Table 1) was greater in the unfiltered SML than unfiltered SSW (0.064 ± 0.062 vs.

184 $0.031 \pm 0.027 \text{ mg L}^{-1} \text{ T-X-100 eq. h}^{-1}$ respectively), whereas mean SA_{temp} was greater in SSW

- than in the SML (0.056 ± 0.031 vs. 0.024 ± 0.054 mg L⁻¹ T-X-100 eq. h⁻¹ respectively). These
- values also show that in unfiltered SML samples, $SA_{irr} > SA_{temp}$, whereas in unfiltered SSW,

187 $SA_{temp} > SA_{irr}$. For the 0.22 µm filtered SML sample, the irradiation effect was slightly greater 188 than the temperature effect (0.030 vs 0.026 mg L⁻¹ T-X-100 eq. h⁻¹).

189

190 A strong correlation between CDOM a_{300} and SA in initial (T₀) samples (τ (11) = 0.745, p =

191 0.001, $R^2 = 0.874$; supporting information), corroborates previous SA and CDOM data from

192 estuaries and the open ocean, where SA and CDOM negatively correlate with salinity (e.g.

193 Pereira et al., 2016, 2018; Uher et al., 2001). In many estuaries photochemical SA production

could be masked by strong lateral SA gradients from the mixing of high SA river water with low

- 195 SA coastal water (Pereira et al., 2016).
- 196

197 CDOM photodegradation (SML and SSW) coincided with SA photoproduction across the

salinity range sampled (0.3-32.0). CDOM is an important seawater surfactant component (e.g.

199 Tilstone, 2010) whose photodegradation in coastal and oceanic waters is widely documented

200 (Mopper et al., 2014). Ten of 12 irradiations where CDOM was quantified showed significant

positive correlations between SA and S_R (p < 0.05 for 10; $R^2 > 0.5$ for six), implying increased

202 SA during irradiation to be consistent with decreasing CDOM molecular weight. We therefore

203 contend that relatively low molecular weight surfactants are a likely by-product of CDOM

204 photodegradation in marine waters.

205

We found moderately strong positive correlations between SA_{irr} and initial $S_{350-400}$ (p = 0.015,

207 $R^2 = 0.546$, supporting information) but not for SA_{temp} , or for a_{300} , $S_{275-295}$ or S_R at T_0 (p \ge

208 0.176 and $R^2 \le 0.098$; data not shown). This suggests that the initial chemical composition and

209 hence reactivity of the CDOM pool, rather than CDOM abundance, impacts rates of SA

210 production during irradiation.



Incubation (h)

Figure 2 Changes in SA during 24-hour irradiations (sites TE1-TE4; Tyne estuary) for three experimental protocols: irradiated samples (IS), dark controls (DC) and temperature controls (TC). Sample designations are: UF (unfiltered); F (0.2 µm PES membrane filtered SML); SML (sea-surface microlayer); SSW (sub-surface water). The salinity of each sample is shown in brackets.

Table 1 SA production rates (mg l^{-1} T-X-100 eq. h^{-1}) estimated over 0-2 hours and 0-24 hours of irradiation for all Tyne estuary samples. SA production due to irradiation (SA_{*irr*}) is the difference in SA (mg l^{-1} T-X-100 eq.) between IS and DC at each timepoint (divided by the appropriate time) and SA production due to temperature (SA_{*temp*}) is the corresponding difference between DC and TC.

		SA (mg l ⁻¹ T-X-100 equivalents h ⁻¹)						
Sample description	Site	2 hours in	cubation	24 hours incubation				
		SA _{irr}	SA _{irr} SA _{temp}		SA _{temp}			
Unfiltered SML	TE1	0.083	-	0.006	-			
(n = 7)	TE1	-0.004	-	0.006	-			
	TE1	0.022	-	0.004	-			
	TE2	0.083	-0.056	0.004	0.008			
	TE3	0.042	0.056	-	0.006			
	TE4	0.035	0.037	0.006	0.000			
	TE1	0.186	0.057	0.010	0.005			
		0.064 ± 0.062 *	-	0.006 ± 0.002 *	-			
	Mean $\pm \sigma$	$0.087\pm0.070~^\dagger$	0.024 ± 0.054 †	$0.007\pm0.003~^\dagger$	0.005 ± 0.003 [†]			
$0.22 \ \mu m$ filtered SML	TE1	0.030	0.026	0.001	0.001			
(n = 1)								
Unfiltered SSW	TE1	0.036	-	0.024	-			
(n = 6)	TE1	0.033	-	0.004	-			
	TE1	0.069	-	0.004	-			
	TE2	-0.006	0.089	0.015	0.007			
	TE3	0.048	0.052	0.005	0.001			
	TE4	0.008	0.027	0.001	0.002			
		0.031 ± 0.025 *	-	0.008 ± 0.009 *	-			
	Mean $\pm \sigma$	0.017 ± 0.028 [†]	0.056 ± 0.031 [†]	$0.007\pm0.007~^\dagger$	$0.003\pm0.003^{\dagger}$			

* Mean and one standard deviation calculated using all available data.

[†]Mean and one standard deviation calculated using only experimental data where temperature controls were included as a sample treatment.

214 **7 Discussion and Implications**

215 We have shown the first evidence of coincident SA photoproduction and CDOM

- 216 photodegradation in marine (estuarine) waters, although photoreactions implicating specific
- components of the marine surfactant pool are well established (e.g. Grzybowski, 2009; Kieber et
- al., 1997; Ortega-Retuerta et al., 2009). Our irradiations showed typical CDOM photobleaching

reflected in decreasing a_{300} and increasing S_R with time, indicative of decreases in dissolved organic matter (DOM) molecular weight.

221

222 Our irradiation data inevitably include a temperature related component due to warming that could cause increases in microbial production (e.g. Kurata et al., 2016) or the interfacial 223 adsorption of surfactants due to entropic effects in the hydration shell (e.g. Gosálvez et al., 2009; 224 Mohajeri & Dehghan Noudeh, 2012; Southall et al., 2001; Tielrooji et al., 2010), or an aggregate 225 226 of both. At higher temperatures, the hydrogen bond network in the hydration shell is more dynamic (Tielrooji et al., 2010). Hence, an increase in temperature increases hydration shell 227 entropy by breaking hydrogen bonds (Southall et al., 2001). Consequently, the size of the 228 hydration shell diminishes, and surfactant adsorption density increases (Gosálvez et al., 2009). 229 230 We contend that changes in surfactant adsorption behaviour are the likely dominant driver of temperature-related SA changes because the SA_{temp} data showed no concomitant changes in 231 CDOM a_{300} or S_R . Microbial processing, adsorption and photodissolution cannot be excluded in 232 these unfiltered water samples. Changes in CDOM spectral characteristics may be used to 233 diagnose CDOM processing: increasing $S_{275-295}$ and S_R , and decreasing $S_{350-400}$ indicate 234 photobleaching, while opposite trends indicate microbial alteration (Helms et al., 2008). 235 However, $S_{350-400}$ changes during irradiations were negligible between sample treatments, 236 suggesting that microbial activity followed the same trend in each. 237 238 A noteworthy feature was that irradiation per se was an independent driver of SA production, 239 where SA_{irr} in the unfiltered SML (0.064 ± 0.062 mg L⁻¹ T-X-100 equivalents h⁻¹) generally 240 exceeded that in unfiltered SSW (0.031 \pm 0.027 mg L⁻¹ T-X-100 equivalents h⁻¹). Overall 241 enrichments in relatively labile DOM compounds are an established feature of coastal systems 242 (e.g. Galgani & Engel, 2016); these compounds transfer to the SML via bubble scavenging 243

(Hardy, 1982; Robinson et al., 2019). Our data support the notion of SA photoproduction, either

- 245 directly via the formation of new surface-active substances, or indirectly by photochemical
- transformations of existing surfactants allowing adsorption to the air-sea interface in greater
- numbers. CDOM photodegradation in parallel with SA photo-production strongly supports thisconcept.
- 249

250 Our data imply potential contributions of SML photochemistry to k_w suppression by surfactants

- 251 (e.g. Brockmann et al., 1982; Frew et al., 1990; Pereira et al., 2016; 2018; Ribas-Ribas et al.,
- 252 2018a; Salter et al., 2011) and to marine boundary layer aerosol and trace gas photochemistry
- 253 (Alpert et al., 2017; Bernard et al., 2016; Brüggemann et al., 2017; Ciuraru et al., 2015a; 2015b;
- Clifford et al., 2008; Fu et al., 2015; Reeser et al., 2009; Rossignol et al., 2016) that demand
- further scrutiny. Pereira et al (2018) applied a positive relationship between sea surface
- temperature (SST) and k_w suppression at the ocean basin scale, implicating daily insolation as a
- driver of surfactant production via primary productivity. Our results indicate that irradiation of
- the SML is a likely important independent driver of SA production in addition to skin layer
- temperature, and consequently is an important independent control on k_w .
- 260

It is instructive to estimate the potential scale of such control, by re-examining k_{660} (k_w for CO₂ in

seawater at 20 °C) estimates for the coastal North Sea (B1-B5; Figure 1), made by Pereira et al.

263 (2016) in a gas exchange tank, that showed strong inverse relationships with SA. We applied

- these to our T_0 irradiation data assuming them to represent in situ SA. This resulted in k_{660} values
- of 0.6-13.4 cm h^{-1} spanning TE1-TE4 (salinity 0.3-32.0) consistent with values found by Pereira

et al (2016) and typical of other coastal sites (e.g. Kremer et al. 2003; Ribas-Ribas et al. 2018b). 267

Table 2. Projected k_{660} (cm h⁻¹) values, based on Pereira et al. (2016), for Tyne estuary SML and SSW SA at 0 hours and 2 hours irradiation (irradiated samples only), over a salinity gradient of 0.3 (TE1) to 32.0 (TE4).

Site	SML proj	ected k660 (cm h ⁻¹):	SSW projected k660 (cm h ⁻¹):			
Site	0-hours	2-hours	Δ (%)	0-hours	2-hours	Δ (%)	
TE1	0.59	1.48	44.1	0.90	2.24	18.9	
TE1	1.45	1.05	28.1	1.81	1.28	29.2	
TE1	2.65	0.43	27.3	2.76	0.75	16.7	
TE1	3.66	1.87	48.9	-	-	-	
TE1*	5.93	4.78	19.5	-	-	-	
TE2	3.20	2.71	15.2	5.04	4.14	17.7	
TE3	4.93	3.15	36.1	4.44	3.49	21.3	
TE4	12.14	9.44	22.2	13.36	11.64	12.9	

* 0.22 µm filtered SML sample.

Given that our most saline SML sample (TE4: salinity 30.5, SA 0.15 mg L^{-1} T-X-100 eq.;

- Figures 1 and 2*f*) was closest to the salinity range (33.1-34.6) given by Pereia et al. (2016) and
- within the respective SA range (0.08-0.38 mg L^{-1} T-X-100 eq.), we extended the Pereira et al.
- (2016) analysis to our 2-hour SA_{IS} data for TE4, which gives k_{660} suppressions of 22.2% (9.4 cm
- 273 h^{-1} at 2-hours; SML) and 12.9% (11.6 cm h^{-1} at 2-hours; SSW) relative to T₀ k_{660} (12.1 and 13.4
- 274 cm h⁻¹ respectively). Overall, unfiltered samples gave k_{660} suppressions of 15.2-48.9% (0.4-9.4
- 275 cm h⁻¹ at 2-hours) in the SML and 12.9-29.3% (0.8-11.6 cm h⁻¹ at 2-hours) in SSW, relative to
- respective $T_0 k_{660}$. Considering the range of k_{660} suppression by surfactants (Pereira et al. 2016),
- 277 gas exchange control driven by photochemical changes could be considerable.
- 278

Due to the proximity of our samples to those of Pereira et al. (2016) (Figure 1), differences in 279 280 organic composition between them, even when accounting for potential temporal variability, are likely to be smaller than contrasts with other geographical regions, and we note that SML 281 surfactant photochemistry is yet to be explored in either oceanic waters or indeed in freshwater 282 systems. Given that SML surfactant pool composition is likely to be important in addition to SA 283 in controlling the magnitude of k_w (Pereira et al. 2016), regional to global differences in the 284 composition of the SML surfactant pool and the attendant temporal variability will likely be 285 reflected in a variable photochemical contribution to k_w control that demands further scrutiny. 286

287 **5 Conclusions**

Adequate parameterization of the factors controlling air-sea gas exchange is a long-standing

- scientific goal deemed essential to predicting global climate change. An increasing scientific
- focus is now on SML surfactant control of k_w (e.g. Brockmann et al., 1982; Frew et al., 1990;
- 291 Pereira et al., 2016; 2018; Ribas-Ribas et al., 2018a; Salter et al., 2011). Temperature is a known

292 control of surfactant adsorption kinetics, but we have shown irradiation to be an additional,

independent driver, in parallel with CDOM photodegradation. We contend that photoinduced

increases in SA will likely impede k_w at the global scale, with implications for the global budgets

- of climate-active gases. Consequently, studies of surfactant photo reactivity in a range of
- estuarine, coastal, and oceanic waters will be important, specifically those that examine how
- 297 differences in total surfactant pool composition might differentially affect photochemistry and
- hence k_w .

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Supporting Information for

Photo-reactivity of surfactants in the sea-surface microlayer and subsurface water of the Tyne estuary, UK

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Introduction

The supporting data presented here details the Tyne estuary (UK) sampling locations, conditions, and respective sample treatments (Table S1 and Figure S1), and shows chromophoric dissolved organic matter (CDOM) changes recorded during irradiation experiments (Figures S2-S5), correlations between in situ salinity (0.3-32.0), CDOM and total surfactant activity (SA; T-X-100 eq. mg l⁻¹) (Figure S6) and the correlation between in situ CDOM and surfactant production due to irradiation (SA_{irr}) (Figure S7). The CDOM indices presented are: the absorption coefficient at 300 nm (a_{300}), spectral slopes (S; nm⁻¹) for the wavelength ranges 275-295 nm ($S_{275-295}$; nm⁻¹) and 350-400 nm ($S_{350-400}$; nm⁻¹), and the spectral slope ratio ($S_R = S_{275-295}/S_{350-400}$) (Helms et al., 2008).

Site ID	Site name	Longitude	Latitude	Date(s) sampled	Depth sampled	F/UF	Salinity	Sunrise	Sunset
								(hh:mm)	(hh:mm)
TE1	Newburn	1°44'42.6"W	54°58'53.8"N	27 June 2016	SML	UF	3.2	04:29	21:49
					SSW	UF	3.0		
				18 July 2016	SML	UF	5.4	04:52	21:31
					SSW	UF	5.5		
				29 August 2016	SML	UF	0.3	06:07	20:05
					SSW	UF	0.3		
				30 January 2017	SML	UF	1.3	08:00	16:39
						F			
TE2	Millennium Bridge	1°35'39.1"W	54°58'22.5"N	14 October 2016	SML	UF	20.7	07:34	18:09
					SSW	UF	19.6		
TE3	Walker	1°31'99.8"W	54°58'66.1"N	25 November 2016	SML	UF	9.1	07:57	15:48
					SSW	UF	9.8		
TE4	Herd Sands	1°25'21.1"W	55°00'36.6"N	2 December 2016	SML	UF	30.5	08:09	15:42
					SSW	UF	32.0		

Table S1. Details of Tyne estuary, UK, sampling sites (TE1-TE4): 1 L of sea-surface microlayer (SML) and 1 L of subsurface water (SSW) were collected in each case, except at TE1 in January 2017 where only SML (2 L) was sampled and split into 0.22 μm filtered (F) (Millex-GP polyethersulfone (PES) membrane) and unfiltered (UF) subsamples.



Figure S1. Global irradiation on horizontal plane at ground level (GHI, W m⁻²) in the Tyne estuary (sites TE1-TE4), UK, for all sampling dates, from Copernicus Atmosphere Monitoring Service (CAMS; <u>copernicus.eu/</u>; 240-4606 nm; Qu et al., 2017). The dotted grey line is the integrated spectral irradiance (247.8 W m⁻²; 250-1050 nm; ILT950, LOT Quantum Design) of the Xe-arc light source used in all irradiation experiments.



Figure S2. Changes in a_{300} during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 µm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.



Figure S3. Changes in $S_{275-295}$ during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 µm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.



Figure S4. Changes in $S_{350-400}$ during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 µm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.



Figure S5. Changes in S_R during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 µm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.



Figure S6. Correlations between in situ total surfactant activity (SA; T-X-100 eq. mg l⁻¹) with chromophoric dissolved organic matter (CDOM) absorption coefficient at 300 nm (a_{300}), and SA and a_{300} with salinity, in Tyne estuary, UK, seasurface microlayer (SML) and subsurface water (SSW) samples over the salinity gradient 0.3-32.0. Error bars show one standard deviation on SA measurements.



0-2 hr SA_{irr} (mg l⁻¹ TX-100 equivalents h⁻¹)

 τ (11) = 0.585, p = 0.015, R² = 0.546

Figure S7. Initial CDOM spectral slope over the wavelength range 350-400 nm ($S_{350-400}$) vs SA due to irradiation (SA_{irr}) calculated for the initial 0-2 hours for unfiltered samples where $SA_{IS} > SA_{DC}$.